

19



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

11 Publication number:

**0 086 445**  
**A1**

12

# EUROPEAN PATENT APPLICATION

21 Application number: 83101194.5

51 Int. Cl.<sup>3</sup>: **H 01 F 1/36, G 03 G 9/10,**  
**C 04 B 35/26**

22 Date of filing: 08.02.83

30 Priority: 12.02.82 JP 20983/82  
12.02.82 JP 20984/82  
12.02.82 JP 20985/82

71 Applicant: **TDK ELECTRONICS CO., LTD.,** 13-1,  
Nihonbashi 1-chome, Chuo-ku Tokyo 103 (JP)

43 Date of publication of application: 24.08.83  
Bulletin 83/34

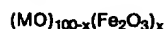
72 Inventor: Imamura, Kenji c/o TDK Electronics Co., Ltd.,  
13-1, Nihonbashi 2-chome, Chuo-ku Tokyo 103 (JP)  
Inventor: Saitoh, Hiroshi c/o TDK Electronics Co., Ltd.,  
13-1, Nihonbashi 1-chome, Chuo-ku Tokyo 103 (JP)  
Inventor: Kakizaki, Katsuhisa c/o TDK Electronics Co.,  
Ltd., 13-1, Nihonbashi 1-chome, Chuo-ku Tokyo 103 (JP)  
Inventor: Makino, Motohiko c/o TDK Electronics Co.,  
Ltd., 13-1, Nihonbashi 1-chome, Chuo-ku Tokyo 103 (JP)

64 Designated Contracting States: **AT BE DE GB IT NL**

74 Representative: **Wächtershäuser, Günter, Dr., Tal 29,**  
**D-8000 München 2 (DE)**

54 **Magnetic carrier powder.**

57 A magnetic carrier powder composed essentially of particles of a ferrite having a composition represented by the formula



where M is Mg, Mn, Zn, Ni, a combination of Mg in an atomic ratio of at least 0.05 with at least one metal selected from the group consisting of Zn, Cu, Mn and Co, a combination of Mn in an atomic ratio of at least 0.05 with at least one metal selected from the group consisting of Zn, Cu, Mg and Co, or a combination of Ni in an atomic ratio of at least 0.05 with at least one metal selected from the group consisting of Zn, Mg, Mn, Cu and Co, and x is greater than 53 molar %.

**EP 0 086 445 A1**

0086445

EA-4146

TDK-208  
(870007)

- 1 -

MAGNETIC CARRIER POWDER

The present invention relates to a magnetic carrier powder. More particularly, the present invention relates to a magnetic carrier powder to be used for magnetic brush development.

It has been proposed to use a so-called soft ferrite as a carrier  
5 powder for magnetic brush development (see, for instance, U.S. Patent No. 3,839,029, No. 3,914,181 or No. 3,929,657).

A carrier powder composed of such a ferrite exhibits magnetic characteristics equal to a conventional iron powder carrier but is not required to provide a coating layer such as a resin layer on its surface  
10 which is required for the iron powder carrier. Therefore, it is far superior in its durability.

The ferrite composition which is practically in use as a conventional carrier powder is represented by the formula  
 $(MO)_{100-x}(Fe_2O_3)_x$  (where M is at least one of divalent metals), x is  
15 at most 53 molar %.

According to the results obtained by the researches conducted by the present inventors, the electric resistance of ferrite powder particles can be varied by controlling the atmosphere for burning even when the ferrite powder particles have the same composition.  
20 By changing the resistance of the carrier powder, it is possible to obtain images having various gradations and to optionally control

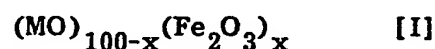
the image quality. Further, the resistance of the carrier powder can be changed to obtain the optimum characteristics for a variety of copying machines.

Accordingly, for the ferrite powder particles, the wider the range  
5 of the electric resistance changeable by the modification of the burning atmosphere, the better.

However, the above-mentioned ferrite composition containing at most 53 molar % of  $\text{Fe}_2\text{O}_3$  has a high resistance value by itself and the image density thereby obtainable is low. Further, even when the  
10 burning atmosphere is modified, the changeable range of the electric resistance is relatively small and accordingly the changeable rate of the gradation is small, whereby the image quality can not optionally be controlled.

Under these circumstances, it is the primary object of the present  
15 invention to provide a ferrite carrier powder composition having a wider changeable range of the electric resistance than that of the conventional ferrite composition.

The present invention provides a magnetic carrier powder composed essentially of particles of a ferrite having a composition represented  
20 by the formula



where M is Mg, Mn, Zn, Ni, a combination of Mg in an atomic ratio of at least 0.05 with at least one metal selected from the group consisting of Zn, Cu, Mn and Co, a combination of Mn in an atomic ratio of  
25 at least 0.05 with at least one metal selected from the group consisting of Zn, Cu, Mg and Co, or a combination of Ni in an atomic ratio of at least 0.05 with at least one metal selected from the group consisting of Zn, Mg, Mn, Cu and Co, and x is greater than 53 molar %.

Now, the present invention will be described in detail with reference to the preferred embodiments.

In the first embodiment of the present invention, M in the formula I is Mg or a combination of Mg in an atomic ratio of at least  
5 0.05 with at least one metal selected from the group consisting of Zn, Cu, Mn and Co.

In the second embodiment, M in the formula I is Mn, Zn or a combination of Mn in an atomic ratio of at least 0.05 with at least one metal selected from the group consisting of Zn, Cu, Mg and Co  
10 provided that Mg is in an atomic ratio of less than 0.05.

According to the third embodiment, M in the formula I is Ni or a combination of Ni in an atomic ratio of at least 0.05 with at least one metal selected from the group consisting of Zn, Mg, Mn, Cu and  
x in the formula I is at least 45 molar %.

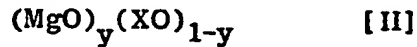
15 Referring to the first and second embodiments, the amount x of iron as  $\text{Fe}_2\text{O}_3$  is greater than 53 molar %. If x is less than 53 molar %, the changeable range of the electric resistance tends to be small. Whereas, especially when x is at least 54 mol %, the changeable range of the electric resistance becomes extremely wide. The upper limit  
20 for x is not critical and may be at any level less than 100 molar %. However, in view of the saturation magnetization, x is preferably at most 99 molar %, more preferably at most 90 molar %, whereby the saturation magnetization becomes extremely great and there will be little possibilities that the carrier deposits on the photosensitive  
25 material or the carrier scatters from the magnetic brush.

On the other hand, in the third embodiment as mentioned above, x is at least 54 molar %. If x is less than 54 molar %, the changeable range of the electric resistance tends to be small. Whereas, especially

when x is at least 55 molar %, the changeable range of the electric resistance becomes extremely wide. As in the case of the first and second embodiments, the upper limit for x is not critical in the third embodiment and may be at any level less than 100 molar %. Likewise, 5 x is preferably at most 99 molar %, more preferably at most 90 molar %, whereby the saturation magnetization becomes extremely great and there will be little possibilities that the carrier deposits on the photosensitive material or the carrier scatters from the magnetic brush.

With respect to M in the formula I, in the first embodiment, 10 M may be composed of Mg alone or a combination of Mg with at least one of Zn, Cu, Mn and Co. When M is such a combination, the atomic ratio of Mg in M is at least 0.05. If the atomic ratio of Mg is less than 0.05, the saturation magnetization tends to decrease and the deposition of the carrier on the photosensitive material or the scattering 15 of the carrier from the magnetic brush tends to increase. Likewise, in the second embodiment, M may be composed of Mn or Zn alone or a combination of Mn with at least one of Zn, Cu, Mg and Co. When M is composed of such a combination, the atomic ratio of Mn in M is at least 0.05. If the atomic ratio of Mn is less than 0.05, the saturation magnetization tends to decrease and the deposition of carrier or 20 the scattering of the carrier as mentioned above tends to increase. Likewise, in the third embodiment, M may be composed of Ni alone or a combination of Ni with at least one of Zn, Mg, Mn, Cu and Co. When M is composed of such a combination, the atomic ratio of Ni in 25 M is at least 0.05. If the atomic ratio of Ni is less than 0.05, the saturation magnetization tends to decrease and the deposition of the carrier or the scattering of the carrier as mentioned above tends to increase.

In a preferred specific example of the first embodiment, MO in the formula I is represented by the formula



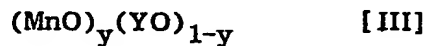
In the formula II, X is Zn or a combination of Zn with at least one of Cu, Mn and Co, and y is at least 0.05 and less than 1.

The ferrite powder having a composition represented by the above formula II gives extremely high saturation magnetization.

In this case, better results are obtainable when y is from 0.05 to 0.99, especially from 0.1 to 0.7. The atomic ratio of Zn in X is preferably 1 or within a range of at least 0.3 and less than 1, whereby extremely high saturation magnetization is obtainable.

When X is a combination of Zn with 2 or 3 elements selected from Cu, Mn and Co, the proportion of Cu, Mn or Co may be optionally selected.

Likewise, in a preferred example of the second embodiment, MO in the formula I is represented by the formula

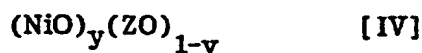


In the formula III, Y is Zn or a combination of Zn with at least one of Cu, Mg and Co, and y is at least 0.05 and less than 1.

The composition represented by the formula III gives extremely high saturation magnetization. In this case, particularly good results are obtainable when y is from 0.05 to 0.99, especially from 0.1 to 0.7.

The atomic ratio of Zn in Y is preferably 1 or within the range of at least 0.3 and less than 1, whereby extremely high saturation magnetization is obtainable. Further, when Y is a combination of Zn with 2 or 3 elements selected from Cu, Mg and Co, the proportion of Cu, Mg or Co may be optionally selected.

Likewise, in a preferred example of the third embodiment,  
MO in the formula I is represented by the formula



In the formula IV, Z is Zn or a combination of Zn with at least  
5 one of the Mg, Mn, Cu and Co and y is at least 0.05 and less than  
1. The composition represented by the formula IV gives extremely  
high saturation magnetization. In this case, particularly good results  
are obtainable when y in the formula IV is from 0.05 to 0.99, especially  
from 0.1 to 0.7. The atomic ratio of Zn in Z is preferably 1 or  
10 within a range of at least 0.3 and less than 1, whereby extremely  
high saturation magnetization is obtainable. When Z is a combination  
of Zn with 2 or 3 elements selected from Mg, Cu, Mn and Co,  
the proportion of Mg, Cu, Mn or Co may be optionally selected.

The ferrite powder particles of the present invention have a  
15 spinel structure. The ferrite powder particles having the above  
mentioned compositions may usually contain upto 5 molar % of an  
oxide of Ca, Bi, Cr, Ta, Mo, Si, V, B, Pb, K, Na or Ba. The ferrite  
powder particles usually have an average particle size of at most  
1000  $\mu\text{m}$ .

20 The ferrite powder particles are useful as a magnetic carrier  
powder as they are prepared i.e. without being coated with a coat-  
ing layer on the surfaces.

The electric resistance of the ferrite powder particles constitut-  
ing the magnetic carrier powder of the present invention is usually  
25 within a range of from  $10^4$  to  $10^{14} \Omega$ , preferably from  $10^5$  to  $10^{12} \Omega$   
as measured in the following manner by application of 100 V.

With the ferrite powder particles of the present invention having  
electric resistance within the above-mentioned range, the resistance

value can continuously be changed by modifying the burning conditions which will be described hereinafter, and the maximum changeable ratio is as high as from  $10^6$  to  $10^{10}$ , whereby an electrostatic image having a desired image quality can optionally be selected.

5        The measurement of the resistance of the ferrite powder particles can be conducted in the following manner in accordance with a magnetic brush development system. Namely, an N-pole and a S-pole are arranged to face each other with a magnetic pole distance of 8 mm so that the surface magnetic flux density of the magnetic poles  
10       becomes 1500 Gauss and the surface area of the facing magnetic poles is 10 x 30 mm. Between the magnetic poles, a pair of non-magnetic flat electrodes are disposed in parallel to each other with an electrode distance of 8 mm. Between the electrodes, 200 mg of a test sample is placed and the sample is held between the electrodes  
15       by the magnetic force. With this arrangement, the electric resistance is measured by an insulating resistance tester or an ampere meter.

      If the resistance measures in such a manner exceeds  $10^{14} \Omega$ , the image density tends to decrease. On the other hand, if the resistance is less than  $10^{14} \Omega$ , the amount of the deposition of the  
20       carrier on the photosensitive material tends to increase and the resolving power and the gradation tend to be deteriorated, whereby the image quality tends to be of high contrast.

      Further, the saturation magnetization  $\sigma_m$  of the ferrite powder particles of the present invention is preferably at least 35 emu/g,  
25       whereby the deposition of the carrier on the photosensitive material or the scattering of the carrier by repeated development operations can be minimized. Better results are obtainable when the saturation magnetization  $\sigma_m$  is at least 40 emu/g.



The magnetic carrier powder composed of such ferrite powder particles may be prepared in such a manner as described in U.S.

Patent No. 3,839,029, No. 3,914,181 or No. 3,926,657.

Namely, firstly, metal oxides are mixed. Then, a solvent such as  
5 water is added and the mixture is slurried, for instance, by means  
of a ball mill. Additives such as a dispersing agent or a binder may  
be added as the case requires. The slurry is then granulated and  
dried by a spray drier. Thereafter, the granules are subjected to  
burning at a predetermined burning temperature in a predetermined  
10 burning atmosphere. The burning may be conducted in accordance  
with a conventional method.

If the equilibrium oxygen partial pressure at the time of the  
burning is reduced, the electric resistance of the ferrite powder  
particles decreases. If the oxygen partial pressure is continuously  
15 changed from the burning atmosphere of air to the burning atmosphere  
of the nitrogen, the electric resistance of the particles can likewise  
continuously be changed.

After the burning, the particles are pulverized or dispersed  
and classified into a desired particle size to obtain a magnetic carrier  
20 powder of the present invention.

The magnetic carrier powder of the present invention is mixed  
with a toner to obtain a developer. The type of the toner to be  
used and the toner concentration are not critical and may optionally  
be selected.

25 Further, the magnetic brush development system to be used to  
obtain an electrostatic copy image and the photosensitive material are  
not critical, and an electrostatic copy image can be obtained in  
accordance with a conventional magnetic brush development method.

By optionally modifying the burning atmosphere in its production, the magnetic carrier powder of the present invention can be prepared to have a wide changeable range of the electric resistance i.e. as wide as from  $10^6$  to  $10^{10}$ . Therefore, it is possible to readily  
5 obtain a carrier powder which is capable of providing an optimum image depending upon the type of the copying machine. Further, the image quality can thereby optionally be selected.

The magnetic carrier powder of the present invention is not required to have a coating on the particle surfaces and accordingly  
10 its durability is excellent.

Furthermore, the saturation magnetization thereby obtained is as high as at least 35 emu/g, whereby the deposition of the carrier on the photosensitive material or the scattering of the carrier can be minimized.

15 Now, the present invention will be described in further detail with reference to Examples.

#### EXAMPLE 1:

Metal oxides were mixed to obtain six different types of compositions (Samples Nos. 1 to 6) as shown in Table 1 in molar ratios  
20 calculated as the divalent metal oxides and  $\text{Fe}_2\text{O}_3$ . Then, one part by weight of water was added to one part by weight of each composition and the mixture was mixed for five hours in a ball mill to obtain a slurry. Appropriate amounts of a dispersing agent and a binder were added thereto. The slurry was then granulated and dried at  
25 a temperature of at least  $150^\circ\text{C}$  by a spray drier.

The granulated product was burned in an air atmosphere and a nitrogen atmosphere, respectively, at a maximum temperature of  $1350^\circ\text{C}$ . Thereafter, the granules were pulverized and classified

to obtain twelve kinds of ferrite powder particles having an average particle size of 45  $\mu\text{m}$ .

Each ferrite powder thereby obtained was subjected to an X-ray analysis and a quantitative chemical analysis whereby it was confirmed that each ferrite powder had a spinel structure and a metal composition corresponding to the initial mixing ratio.

Then, the saturation magnetization  $\sigma_m$  (emu/g) of each ferrite powder and its electrical resistance ( $\Omega$ ) upon application of 100 V were measured. The saturation magnetization  $\sigma_m$  was measured by a magnetometer of a sample vibration type. The measurement of the electric resistance was conducted in the above-mentioned manner wherein the resistance of the 200 mg of the sample when 100 V was applied was measured by an insulation resistance meter.

For each composition,  $(\sigma_m)_N$  for the burning in the nitrogen atmosphere,  $(\sigma_m)_A$  for the burning in the air atmosphere, the resistance  $R_A$  for the burning in the air atmosphere, the resistance  $R_N$  for the burning in the nitrogen atmosphere and the resistance changing ratio  $R_A/R_N$  are shown in Table 1.

Further, each ferrite powder was by itself used as a magnetic carrier powder. Namely, it was mixed with a commercially available two-component toner (an average particle size of  $11.5 \pm 1.5 \mu\text{m}$ ) to obtain a developer having a toner concentration of 11.5% by weight. With use of each developer, magnetic brush development was carried out by means of a commercially available electrostatic copying machine. The surface magnetic flux density of the magnet roller for the magnetic brush development was 1000 Gauss and the rotational speed of the magnet roller was 90 rpm. The distance between magnet roller and the photosensitive material was  $4.0 \pm 0.3 \text{ mm}$ . As the photosensitive material, a selenium photosensitive material was used and

the maximum surface potential thereof was 800 V. With use of a Grey scale made by Eastman Kodak Co., a toner image was obtained on an ordinary paper sheet by means of the above-mentioned electrostatic copying machine. The image density (ID) with the original  
5 density (OD) being 1.0 was obtained, and the difference between (ID)<sub>N</sub> of the particles obtained by the burning in the nitrogen atmosphere and (ID)<sub>A</sub> of the particles obtained by the burning in the air atmosphere was obtained.

The results thereby obtained are shown in Table 1.

10 In almost all cases of the magnetic carrier powders, the deposition of the carrier on the photosensitive material or scattering of the carrier was scarcely observed.

0086445

- 12 -

Table 1

Sample No.	Present invention				Comparative Samples	
	1	2	3	4	5	6
<b>Composition (molar %)</b>						
MgO	6	10.5	14.5	18.5	19.5	23
ZnO	10	20	20	20	20	20
CuO	4	7.5	7.5	7.5	7.5	7.5
Fe <sub>2</sub> O <sub>3</sub>	80	62	58	54	53	49.5
<b>Saturation magnetization (emu/g)</b>						
( $\sigma_m$ ) <sub>N</sub>	95	85	85	70	70	46
( $\sigma_m$ ) <sub>A</sub>	65	62	55	50	50	46
<b>Electric resistance (<math>\Omega</math>)</b>						
R <sub>N</sub>	10 <sup>4</sup>	10 <sup>5</sup>	10 <sup>6</sup>	10 <sup>8</sup>	10 <sup>9</sup>	10 <sup>2</sup>
R <sub>A</sub>	10 <sup>12</sup>	10 <sup>12</sup>	10 <sup>12</sup>	10 <sup>12</sup>	10 <sup>12</sup>	10 <sup>12</sup>
R <sub>A</sub> / R <sub>N</sub>	10 <sup>8</sup>	10 <sup>7</sup>	10 <sup>6</sup>	10 <sup>4</sup>	10 <sup>3</sup>	10 <sup>2</sup>
(ID) <sub>N</sub> - (ID) <sub>A</sub>	1.0	1.0	0.9	0.7	0.3	0.2

From the results shown in Table 1, it is evident that the magnetic carrier powders of the present invention with a  $\text{Fe}_2\text{O}_3$  content x of greater than 53 molar % have extremely great changing ratios of the resistance, whereby the gradation of the image can be modified to a great extent and the range of the free choice of the image quality is extremely wide.

Further, in the above Example, a mixture of air and nitrogen was used as a burning atmosphere and the mixing ratio was varied, whereby it was confirmed that the resistance and the image density varies continuously between the values presented above.

EXAMPLE 2:

In the same manner in the Example 1, magnetic carrier powders were prepared to have the compositions as shown in Tables 2 and 3 and the above-mentioned  $R_A$ ,  $R_N$ ,  $R_A/R_N$  and  $(ID)_N - (ID)_A$  were measured.

The results are shown in Tables 2 and 3.

Table 2

Sample No.	Composition (molar %)	$R_A$ ( $\Omega$ )	$R_N$ ( $\Omega$ )	$R_A / R_N$	$(ID)_N - (ID)_A$
7(Comparative)	$\left[ \begin{array}{l} (MgO)_{0.04}(ZnO)_{0.96} \\ (MgO)_{0.04}(ZnO)_{0.96} \end{array} \right] \left\{ \begin{array}{l} 50.5(Fe_2O_3)_{49.5} \\ 47(Fe_2O_3)_{53} \end{array} \right\} \sigma_m < 20 \text{emu/g}$	$10^{12}$	$10^{10}$	$10^2$	0.2
8(Comparative)		$10^{12}$	$10^7$	$10^5$	0.7
8(Comparative)	$\begin{array}{l} (MgO)_{31.5}(ZnO)_{19}(Fe_2O_3)_{49.5} \\ (MgO)_{25}(ZnO)_{15}(Fe_2O_3)_{60} \end{array}$	$10^{13}$	$10^{10}$	$10^3$	0.3
9(Present invention)		$10^{13}$	$10^6$	$10^7$	0.9
10(Comparative)	$\begin{array}{l} (MgO)_{10.5}(ZnO)_{20}(MnO)_{20}(Fe_2O_3)_{49.5} \\ (MgO)_{9.3}(ZnO)_{15.7}(MnO)_{20}(Fe_2O_3)_{55} \end{array}$	$10^{12}$	$10^9$	$10^3$	0.3
11(Present invention)		$10^{12}$	$10^7$	$10^5$	0.8
12(Comparative)	$\begin{array}{l} (MgO)_{25}(ZnO)_{25}(CoO)_1(Fe_2O_3)_{49} \\ (MgO)_{19.6}(ZnO)_{19.4}(CoO)_1(Fe_2O_3)_{60} \end{array}$	$10^{13}$	$10^{11}$	$10^2$	0.2
13(Present invention)		$10^{13}$	$10^6$	$10^7$	1.0
14(Comparative)	$\begin{array}{l} (MgO)_{25}(ZnO)_{20}(MnO)_{2.5}(CuO)_3(Fe_2O_3)_{49.5} \\ (MgO)_{18.8}(ZnO)_{13.7}(MnO)_{2.5}(CuO)_3(Fe_2O_3)_{62} \end{array}$	$10^{12}$	$10^9$	$10^3$	0.3
15(Present invention)		$10^{12}$	$10^5$	$10^7$	0.9

Table 3

Sample No.	Composition (molar %)	$R_A (\Omega)$	$R_N (\Omega)$	$R_A / R_N$	$(ID)_N - (ID)_A$
16 (Comparative)	$(MgO)_{20}(ZnO)_{20}(MnO)_5(CuO)_8(Fe_2O_3)_{49}$	$10^{13}$	$10^{11}$	$10^2$	0.2
17 (Present Invention)	$(MgO)_{10}(ZnO)_{20}(MnO)_{3.9}(CuO)_{6.1}(Fe_2O_3)_{60}$	$10^{13}$	$10^7$	$10^5$	0.8
18 (Comparative)	$(MgO)_{10}(ZnO)_{20}(MnO)_{20}(CoO)_1(Fe_2O_3)_{49}$	$10^{13}$	$10^{11}$	$10^2$	0.2
19 (Present Invention)	$(MgO)_{3.9}(ZnO)_{15}(MnO)_{0.1}(CoO)_1(Fe_2O_3)_{80}$	$10^{13}$	$10^3$	$10^7$	1.0
20 (Comparative)	$(MgO)_{10}(ZnO)_{20}(MnO)_{10}(CoO)_1(Fe_2O_3)_{49}$	$10^{13}$	$10^{10}$	$10^3$	0.3
21 (Present Invention)	$(MgO)_{8.8}(ZnO)_{20}(MnO)_{5.2}(CoO)_1(Fe_2O_3)_{55}$	$10^{13}$	$10^7$	$10^6$	0.9
22 (Comparative)	$(MgO)_{20}(ZnO)_{23}(MnO)_2(CuO)_4(CoO)_1(Fe_2O_3)_{50}$	$10^{12}$	$10^9$	$10^3$	0.3
23 (Present Invention)	$(MgO)_{18}(ZnO)_{20}(MnO)_2(CuO)_4(CoO)_1(Fe_2O_3)_{55}$	$10^{12}$	$10^7$	$10^5$	0.8



The effects of the present invention are evident from the results shown in Tables 2 and 3.

With Samples Nos. 8' to 23 ,  $\sigma_m$  of at least 40 emu/g was obtained, whereby no substantial deposition of the carrier on the photosensitive material or no substantial scattering of the carrier was observed. Whereas, Samples Nos. 7 and 8 had  $\sigma_m$  of less than 20 emu/g and substantial deposition of the carrier and substantial scattering of the carrier were observed.

EXAMPLE 3:

10        Samples Nos. 24 to 29 were prepared in the same manner as in Example 1 except that instead of the tunnel furnace, a rotary kiln was used for the burning. The physical properties of the samples were measured in the same manner in Example 1. The compositions of the samples and their physical properties are shown in Table 4. Further, most of the magnetic carrier  
15        powders did not substantially deposit on the photosensitive material and no substantial scattering of the carrier was observed. However, Samples Nos. 28 and 29 containing 53 molar % or less of  $\text{Fe}_2\text{O}_3$  which were burned in air had  $\sigma_m$  of 40 emu/g or less,  
20        whereby the deposition of the carrier on the photosensitive material and the scattering of the carrier were observed.

Table 4

Sample No.	Present invention				Comparative Samples	
	24	25	26	27	28	29
Composition (molar %)						
MnO	15	28.5	31.5	34.5	35.2	39.9
ZnO	5	9.5	10.5	11.5	11.8	12.6
Fe <sub>2</sub> O <sub>3</sub>	80	62	58	54	53	49.5
$\sigma_m$ (emu/g)	85	80	72	66	64	45
R <sub>A</sub> ( $\Omega$ )	10 <sup>12</sup>	10 <sup>12</sup>	10 <sup>12</sup>	10 <sup>12</sup>	10 <sup>12</sup>	10 <sup>12</sup>
R <sub>N</sub> ( $\Omega$ )	10 <sup>5</sup>	10 <sup>5</sup>	10 <sup>6</sup>	10 <sup>7</sup>	10 <sup>9</sup>	10 <sup>9</sup>
R <sub>A</sub> / R <sub>N</sub>	10 <sup>7</sup>	10 <sup>7</sup>	10 <sup>6</sup>	10 <sup>5</sup>	10 <sup>3</sup>	10 <sup>3</sup>
(ID) <sub>A</sub> - (ID) <sub>N</sub>	1.0	1.0	0.9	0.8	0.3	0.3

From the results shown in Table 4, it is evident that the magnetic carrier powders of the present invention containing more than 53 molar % of  $\text{Fe}_2\text{O}_3$  have extremely great changing ratios of the resistances, whereby the gradation of the image can greatly be varied and the range for free choice of the image quality is extremely wide.

In the above Example, a mixture of air and nitrogen was used as the burning atmosphere and the mixing ratio was varied, whereby it was confirmed that the electric resistance and the image density were varied continuously between the values presented above.

EXAMPLE 4:

In the same manner as in Example 1, magnetic carrier powders were prepared to have the compositions as shown in Table 5 and the above-mentioned  $R_A$ ,  $R_N$ ,  $R_A/R_N$  and  $(ID)_N - (ID)_A$  were measured. The results thereby obtained are shown in Table 5.

Table 5

Sample No.	Composition (molar %)	$R_A$ ( $\Omega$ )	$R_N$ ( $\Omega$ )	$R_A / R_N$	$(ID)_N - (ID)_A$
30(Comparative)	$[(MnO)_{0.04}(ZnO)_{0.96}]_{50.5}(Fe_2O_3)_{49.5}$	$10^{12}$	$10^{10}$	$10^2$	0.2
31(Comparative)	$[(MnO)_{0.04}(ZnO)_{0.96}]_{47}(Fe_2O_3)_{53}$	$10^{12}$	$10^7$	$10^5$	0.7
32(Comparative)	$(MnO)_{23}(ZnO)_{20}(CuO)_8(Fe_2O_3)_{49}$	$10^{13}$	$10^{11}$	$10^2$	0.2
33(Present invention)	$(MnO)_{20.3}(ZnO)_{20}(CuO)_{4.7}(Fe_2O_3)_{55}$	$10^{13}$	$10^6$	$10^7$	1.0
34(Comparative)	$(MnO)_{24}(ZnO)_{20}(CuO)_7(MgO)_2(Fe_2O_3)_{47}$	$10^{13}$	$10^{11}$	$10^2$	0.2
35(Present invention)	$(MnO)_{18.8}(ZnO)_{14.2}(CuO)_7(MgO)_2(Fe_2O_3)_{58}$	$10^{13}$	$10^6$	$10^7$	1.0
36(Comparative)	$(MnO)_{20}(ZnO)_{25}(CuO)_5(CoO)_1(Fe_2O_3)_{49}$	$10^{12}$	$10^{10}$	$10^2$	0.2
37(Present invention)	$(MnO)_{14.9}(ZnO)_{17.1}(CuO)_5(CoO)_1(Fe_2O_3)_{62}$	$10^{12}$	$10^5$	$10^9$	1.0
38(Comparative)	$(MnO)_{25.5}(ZnO)_{25.5}(Fe_2O_3)_{49}$	$10^{13}$	$10^{11}$	$10^3$	0.2
39(Present invention)	$(MnO)_{10}(ZnO)_{10}(Fe_2O_3)_{80}$	$10^{13}$	$10^4$	$10^6$	1.1

The effects of the present invention are evident from the results shown in Table 5.

Further, with Samples Nos. 32 to 39,  $\sigma_m$  of at least 40 emu/g was obtained, whereby no substantial deposition of the carrier on the photosensitive material or no substantial scattering of the carrier were observed. Whereas, Samples Nos. 31 to 32 had  $\sigma_m$  of 20 emu/g or less, whereby substantial deposition of the carrier and substantial scattering of the carrier were observed.

EXAMPLE 5:

10        Samples Nos. 40 to 44 were prepared in the same manner as in Example 1 except that the burning was conducted at the maximum temperature of 1300°C. The properties of the samples were measured in the same manner as in Example 1. The compositions of the samples and their properties are shown in Table 6.

15        Each magnetic carrier powder did not show substantial deposition on the photosensitive material and no substantial scattering of the carrier was observed.

Table 6

Sample No.	Present invention			Comparative Samples	
	40	41	42	43	44
Composition (molar %)					
NiO	6	10.5	17.5	19.5	23
ZnO	10	20	20	20	20
CuO	3	6.5	6.5	6.5	6.5
MnO					
Fe <sub>2</sub> O <sub>3</sub>	80	62	55	53	49.5
( $\sigma_m$ ) <sub>N</sub> (emu/g)	85	60	55	50	45
( $\sigma_m$ ) <sub>A</sub> (emu/g)	60	60	50	50	45
R <sub>A</sub> ( $\Omega$ )	10 <sup>12</sup>	10 <sup>13</sup>	10 <sup>14</sup>	10 <sup>14</sup>	10 <sup>14</sup>
R <sub>N</sub> ( $\Omega$ )	10 <sup>4</sup>	10 <sup>5</sup>	10 <sup>6</sup>	10 <sup>11</sup>	10 <sup>12</sup>
R <sub>A</sub> / R <sub>N</sub>	10 <sup>8</sup>	10 <sup>8</sup>	10 <sup>8</sup>	10 <sup>3</sup>	10 <sup>2</sup>
(ID) <sub>A</sub> - (ID) <sub>N</sub>	1.0	1.0	1.0	0.3	0.2

From the results shown in Table 6, it is evident that the magnetic powders of the present invention containing more than 53 mole % of  $\text{Fe}_2\text{O}_3$  have extremely great changing ratios  $R_A/R_N$ , whereby the gradation of the image can be greatly varied and the range for free choice of image quality is extremely wide.

Further, in the above Example, a mixture of air and nitrogen was used as the burning atmosphere and the mixing ratio was varied, whereby it was confirmed that the electric resistance and the image density were varied continuously between the values presented above.

EXAMPLE 6:

In the same manner as in Example 1, magnetic carrier powders were prepared to have the compositions as shown in Table 7 and the above mentioned  $R_A$ ,  $R_N$ ,  $R_A/R_N$  and  $(ID)_N - (ID)_A$  were measured. The results thereby obtained are shown in Table 7.

Table 7

Sample No.	Composition (molar %)	$R_A$ ( $\Omega$ )	$R_N$ ( $\Omega$ )	$R_A / R_N$	$(ID)_N - (ID)_A$
45(Comparative)	$(NiO)_{22.3}(ZnO)_{24.7}(Fe_2O_3)_{53}$	$10^{13}$	$10^8$	$10^5$	0.3
46(Present invention)	$(NiO)_{18}(ZnO)_{20}(Fe_2O_3)_{62}$	$10^{13}$	$10^5$	$10^8$	1.1
47(Comparative)	$[ (NiO)_{0.04}(ZnO)_{0.96} ]_{49}(Fe_2O_3)_{53}$	$10^{14}$	$10^8$	$10^6$	0.4
48(Comparative)	$[ (NiO)_{0.04}(ZnO)_{0.96} ]_{38}(Fe_2O_3)_{62}$	$10^{14}$	$10^5$	$10^9$	1.1
49(Comparative)	$(NiO)_{20}(ZnO)_{20}(MgO)_{10}(Fe_2O_3)_{50}$	$10^{14}$	$10^{11}$	$10^3$	0.3
50(Present invention)	$(NiO)_{18}(ZnO)_{18}(MgO)_9(Fe_2O_3)_{55}$	$10^{14}$	5	9	1.1
51(Comparative)	$(NiO)_{15}(ZnO)_{15}(MgO)_5(MnO)_5(Fe_2O_3)_{50}$	$10^{12}$	$10^8$	$10^4$	0.3
52(Present invention)	$(NiO)_{12}(ZnO)_{20}(MgO)_4(MnO)_4(Fe_2O_3)_{80}$	$10^{12}$	$10^4$	$10^8$	1.0
53(Comparative)	$(NiO)_{25}(ZnO)_{20}(CuO)_5(Fe_2O_3)_{50}$	$10^{12}$	$10^9$	$10^3$	0.3
54(Present invention)	$(NiO)_{20}(ZnO)_{16}(CuO)_4(Fe_2O_3)_{80}$	$10^{12}$	$10^4$	$10^8$	1.0
55(Comparative)	$(NiO)_{25}(ZnO)_{20}(MnO)_2(CuO)_3(Fe_2O_3)_{50}$	$10^{12}$	$10^{10}$	$10^2$	0.2
56(Present invention)	$(NiO)_{20}(ZnO)_{16}(MnO)_{1.6}(CuO)_{2.4}(Fe_2O_3)_{80}$	$10^{12}$	$10^5$	$10^7$	1.0
57(Comparative)	$(NiO)_{20}(ZnO)_{20}(CuO)_2(MgO)_5(MnO)_2(CoO)_1(Fe_2O_3)_{50}$	$10^{14}$	$10^{11}$	$10^3$	0.3
58(Present invention)	$(NiO)_{18}(ZnO)_{18}(CuO)_{1.8}(MgO)_{4.5}(MnO)_{1.8}(CoO)_{0.9}(Fe_2O_3)_{55}$	$10^{14}$	$10^6$	$10^8$	1.0

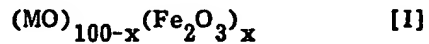


The effects of the present invention are evident from the results shown in Table 7.

Further, with Samples Nos. 45, 46 and 49 to 58,  $\sigma_m$  of at least 40 emu/g was obtained, whereby no substantial deposition of the carrier of the photosensitive material or the scattering of the carrier was observed. Whereas, Samples Nos. 47 and 48 had  $\sigma_m$  of 20 emu/g and substantial deposition of the carrier on the photosensitive material and substantial scattering of the carrier were observed.

## CLAIMS:

1. A magnetic carrier powder composed essentially of particles of a ferrite having a composition represented by the formula



5 where M is Mg, Mn, Zn, Ni, a combination of Mg in an atomic ratio of at least 0.05 with at least one metal selected from the group consisting of Zn, Cu, Mn and Co, a combination of Mn in an atomic ratio of at least 0.05 with at least one metal selected from the group consisting of Zn, Cu, Mg and Co, or a combination of Ni in an atomic ratio of  
10 at least 0.05 with at least one metal selected from the group consisting of Zn, Mg, Mn, Cu and Co, and x is greater than 53 molar %.

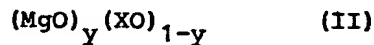
2. The magnetic carrier powder according to Claim 1 wherein M in the formula I is Mg or a combination of Mg in an atomic ratio of at least 0.05 with at least one metal selected from the group consisting  
15 of Zn, Cu, Mn and Co.

3. The magnetic carrier powder according to Claim 1 wherein M in the formula I is Mn, Zn or a combination of Mn in an atomic ratio of at least 0.05 with at least one metal selected from the group consisting of Zn, Cu, Mg and Co provided that Mg is in an atomic ratio of less  
20 than 0.05.

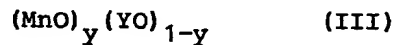
4. The magnetic carrier powder according to Claim 1 wherein M in the formula I is Ni or a combination of Ni in an atomic ratio of at least 0.05 with at least one metal selected from the group consisting of Zn, Mg, Mn, Cu and Co and x in the formula I is at least  
25 54 molar %.

5. The magnetic carrier powder according to Claim 1 wherein x in the formula I is at most 99 molar % and preferably at most 90 molar %.

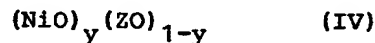
6. The magnetic carrier powder according to Claim 1, wherein MO in the formula I is represented by the formula



where X is Zn or a combination of Zn in an atomic ratio of at least 0.3 with at least one metal selected from the group consisting of Cu, Mn and Co, and y is from 0.05 to 0.99 or by the formula



where Y is Zn or a combination of Zn in an atomic ratio of at least 0.3 with at least one metal selected from the group consisting of Cu, Mg and Co and y is from 0.05 to 0.99 or by the formula



where Z is Zn or a combination of Zn in an atomic ratio of at least 0.3 with at least one metal selected from the group consisting of Mg, Mn, Cu and Co and y is from 0.05 to 0.99.

7. The magnetic carrier powder according to Claim 6, wherein y in the formula IV is from 0.1 to 0.7.

8. The magnetic carrier powder according to Claim 1 wherein the ferrite contains at most 5 molar % of an oxide of Ca, Bi, Cr, Ta, Mo, Si, V, B, Pb, K, Na or Ba.

9. The magnetic carrier powder according to Claim 1 wherein the ferrite particles have an average particle size of at most 1000  $\mu\text{m}$ .

10. The magnetic carrier powder according to Claim 1 wherein the ferrite particles have an electric resistance

of from  $10^4$  to  $10^{14} \Omega$  or preferably  $10^5$  to  $10^{12} \Omega$   
when 100 V is applied.

11. The magnetic carrier powder according to Claim 1 wherein the ferrite particles have saturation magnetization  $\sigma_m$  of at least 35 emu/g or preferably at least 40 emu/g.



European Patent  
Office

# EUROPEAN SEARCH REPORT

0086445

Application number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 83101194.5
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
A	<p><u>EP - A1 - 0 010 732</u> (TDK ELEC-TRONICS)</p> <p>* Claims 1-7; examples *</p> <p>--</p>	1-6	<p>H 01 F 1/36</p> <p>G 03 G 9/10</p> <p>C 04 B 35/26</p>
D,A	<p><u>US - A - 3 929 657</u> (JONES)</p> <p>* Totality *</p> <p>--</p>	1-6	
A	<p><u>US - A - 4 042 518</u> (JONES)</p> <p>* Claim *</p> <p>--</p>	1-6	
A	<p><u>GB - A - 751 623</u> (STEATITE RE-SEARCH CORPORATION)</p> <p>--</p>		
A	<p><u>AT - B - 293 036</u> (N.V. PHILIPS)</p> <p>--</p>		
A	<p><u>DE - B2 - 2 320 883</u> (TDK ELEC-TRONICS)</p> <p>--</p>		<p>TECHNICAL FIELDS SEARCHED (Int. Cl. 7)</p> <p>H 01 F 1/00</p> <p>G 03 G 9/00</p> <p>C 04 B 35/00</p> <p>G 11 B 5/00</p>
D,A	<p><u>US - A - 3 839 029</u> (BERG et al.)</p> <p>--</p>		
D,A	<p><u>US - A - 3 914 181</u> (BERG et al.)</p> <p>----</p>		
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 20-05-1983	Examiner TSILIDIS
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone</p> <p>Y : particularly relevant if combined with another document of the same category</p> <p>A : technological background</p> <p>O : non-written disclosure</p> <p>P : intermediate document</p> <p>T : theory or principle underlying the invention</p> <p>E : earlier patent document, but published on, or after the filing date</p> <p>D : document cited in the application</p> <p>L : document cited for other reasons</p> <p>&amp; : member of the same patent family, corresponding document</p>			